Hierarchical nanocomposite electrocatalyst of bimetallic zeolitic imidazolate framework and MoS$_2$ sheets for non-Pt methanol oxidation and water splitting

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ABSTRACT

We have explored a nanocomposite composed of a bimetallic CoNi-zeolitic imidazole framework embedded by MoS$_2$ nanosheets (MoS$_2$@CoNi-ZIF), as a bifunctional electrocatalyst for non-Pt methanol oxidation reaction (MOR) and overall water splitting in an alkaline solution. The series of MoS$_2$@CoNi-ZIF nanocomposites exhibit different catalytic activities. Significantly, the MoS$_2$@CoNi-ZIF nanosheet with a ratio of MoS$_2$:CoNi-ZIF = 3:1 (MoS$_2$@CoNi-ZIF(3-1)) shows the excellent electrocatalytic activity for MOR, affording an oxidation potential at 1.6 V, also with high catalytic current density and durability. Moreover, the MoS$_2$@CoNi-ZIF(3-1) nanocomposite shows a superior electrocatalytic performance toward HER and OER. When the MoS$_2$@CoNi-ZIF(3-1) was applied as the bifunctional catalyst for both the anode and cathode, the voltage applied to a two-electrode cell is 1.55 V to achieve a current density of 10 mA cm^{-2} for overall water splitting. This work provides a promising electrocatalyst for developing high-performance non-Pt-based clean energy and fuel cells in alkaline solution.

1. Introduction

The demand for efficient energy conversion and storage systems has boosted considerable research efforts on developing novel electrocatalysts applied in the fields of advanced energy devices. A direct methanol fuel cell (DMFC) has employed to settle the present energy crisis by an environmentally friendly way. In DMFCs, methanol oxidation reaction (MOR) is a key step in the exploitation of fuel cell technology, where the precious metal platinum (Pt) exhibits the best catalytic activity [1]. However, the high cost, CO poisoning effect, and slow MOR kinetics are the main disadvantages of Pt-based electrocatalysts, thereby hampering their commercialization applications. As a result, researchers have recently devoted to develop alternative non-noble metal MOR electrocatalysts with highly activity and CO poisoning tolerance. Also, as one of the renewable energy sources, hydrogen (H$_2$) can be achieved by electrochemical water splitting [2]. Nevertheless, the practical application of electrochemical water splitting for H$_2$ production is quite limited because the electrocatalytic efficiency of water splitting is depended on hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Among them, the OER is always limited by its slow sluggish kinetics and the need of a large overpotential [3]. Normally, Pt and RuO$_2$ are mostly applied as the electrocatalysts for HER and OER, respectively. Howbeit, their scarce supply and high cost largely limit their practical exploitation. Furthermore, constructing bifunctional electrocatalysts for both OER and HER in a whole water-splitting cell is still challenging because of the mismatch of high concentrations of H$^+$ and OH$^-$ [4]. To overcome these issues, the development of non-precious-based catalysts with both excellent catalytic activity and high conductivity remains a great challenge. Transition metals and their derivatives are highly efficient alternatives in the field of clean and sustainable energy [3]. NiCo$_2$O$_4$ [5], Ni$_{0.75}$Cu$_{0.25}$ alloy [6], Mn doped Ni(OH)$_2$ [7] *etc* have been employed as anodic materials in MOR while transition metal chalcogenides, oxides/hydroxides, nitrides phosphides, and some metal-free materials have been used for overall water splitting [8]. However, their fabrication processes are usually very complicated, or additives are needed to deteriorate their performances.

Recent studies have shown that the active sites of electrocatalysts are often located in micro- and mesopores whereas the macro-pores are favorable to diffusion of species [9]. Therefore, porous materials are

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considered to be ideal electrocatalyst candidates with high catalytic activity. Metal−organic frameworks (MOFs) have been regarded as ideal precursors or sacrificial templates to fabricate porous functional materials with promising applications in electrochemical aptasensors [10], Li-ion batteries [11], and photocatalysts and so on [12]. As a subclass of MOFs, zeolitic imidazole frameworks (ZIFs), have been emerged as suitable precursors for the development of structure-tailored nanocarbon frameworks due to their abundant pores, versatile surfaces, and high specific surface areas [13]. In particular, a Co-based ZIF, ZIF-67, with imidazolate as linkers has been used to synthesize various Co-containing electrocatalysts [14]. Moreover, Xiao et al. have fabricated cobalt-based bimetallic phosphide ultrathin nanosheets (CoM-P-NS, M = Ni, Mn, Cu, Zn) for highly efficient oxygen evolution in alkaline media [15]. Wen et al. have reported an MXene supported CoNi-ZIF-67 hybrid (CoNi-ZIF-67@$Ti_3C_2T_x$) as an excellent OER electrocatalyst through in-situ growth of bimetallic CoNi-ZIF-67 rhombic dodecahedrons on the $Ti_3C_2T_x$ matrix [16]. Nevertheless, these materials only can be employed as a single catalyst, not bi- or tri-functional catalyst. In fact, there is no successful example for the use of ZIF as MOR catalyst. Besides, it is worthwhile to note that most bifunctional water splitting electrocatalysts have been synthesized by combining the doping of rare metal ions and calcining at high temperatures, further requiring costly electrocatalysts and tedious preparation procedures [17].

To improve the catalytic efficiency, a catalyst with large amounts of active sites and porous nanostructure for the fast transfer of electrons or ions can be developed by optimizing the morphology and composition [18]. Ultrathin two-dimensional (2D) nanosheets (NSs) exhibit excellent catalytic performances because of highly intrinsic activity and ultrahigh specific surface area [14]. Owing to homogeneous chemical composition and unique porous structure, a family of Co-based bimetallic phosphide NSs (CoM-P-NS, M = Ni, Mn, Cu and Zn) have been fabricated using ultrathin MOF NSs as precursors, giving abundant active sites, fast mass transport, and dynamic modulations toward OER [15]. A 2D-layered composite composed of metallic Co and N-carbon exhibits a low overpotential of 103 mV (*vs.* reversible hydrogen electrode (RHE)) at 10 mA cm^{-2}, along with a high cycle durability and a considerable long-term stability for HER [19]. Nevertheless, pure 2D MOFs have been rarely used as electrocatalysts without post-treatment or calcination due to the inferior electrocatalytic activity. Therefore, effective strategies should be developed to fabricate ultrathin 2D MOF-based composite NSs, which can not only enlarge the 2D material family but also boost their practical applications in energy fields. Howbeit, only Co-MOF/graphene oxide composite [20], Cu-MOF [21], and electro-active pyridine-containing MOFs [22] have been explored to catalyze MOR. Thus, it is extremely interesting to develop multifunctional electrocatalysts for overall water splitting and MOR *via* a feasible approach. Additionally, MoS_2, as a typical transition metal sulfide, is regarded as a promising catalyst, especially toward HER, because of its good chemical stability, low cost, and excellent electrocatalytic properties [23,24]. Howbeit, the electrocatalytic activity of MoS_2 may be limited by feasible aggregation and weak conductivity. Enhancing the electrical conductivity or synthesizing MoS_2 nanoarchitectures is highly urgent [25].

Based on above analysis, CoNi-ZIF and MoS_2 NSs may be combined to construct a novel multifunctional catalyst without further treatment. In this work, we have proposed a series of hierarchical nanostructured composites of bimetallic CoNi-ZIF and MoS_2 NSs (MoS_2@CoNi-ZIF) and first explored them as the trifunctional electrocatalysts for MOR, HER, and OER in an alkaline solution (Scheme 1). The electrocatalytic activity of MoS_2@CoNi-ZIF composite with a MoS_2:CoNi-ZIF ratio of 3:1 (MoS_2@CoNi-ZIF(3-1)) outperforms others, including MoS_2, CoNi-ZIF, MoS_2@CoNi-ZIF(1-1), and MoS_2@CoNi-ZIF(5-1). The proposed MoS_2@CoNi-ZIF(3-1) catalyst shows three advantages, namely, (i) multiple catalytic performances for MOR with an oxidation potential of 1.6 V and for water splitting with a low potential of 1.55 V to achieve a

stable current density of 10 mA cm^{-2} in an alkaline solution, (ii) synthesis without requiring calcination or other treatments, and (iii) strong synergistic effect among CoNi-ZIF, metal oxide, and MoS_2, providing the MoS_2@CoNi-ZIF catalyst with a comprehensive performance and high stability in aqueous solution.

2. Experimental section

2.1. Reagents and materials

Cobaltous nitrate (Co(NO$_3$)$_2$·6H$_2$O), nickelous nitrate (Ni(NO$_3$)$_2$·6H$_2$O), and 2-methylimidazole (C$_4$H$_6$N$_2$) were purchased from Aladdin Chemical Reagent Co. Ltd. (Shanghai, China). Sodium molybdate (Na$_2$MoO$_4$·2H$_2$O), thioacetamide (CH$_3$CSNH$_2$), potassium hydroxide (KOH), ethanol (C$_2$H$_5$OH), and methanol (CH$_3$OH) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All reagents were of analytical grade and used without further purification.

2.2. Synthesis of MoS$_2$ NSs

MoS$_2$ NSs were prepared according to the literature [26]. In brief, 50 mg Na$_2$MoO$_4$·2H$_2$O was dissolved in 20 mL of Milli-Q water, while 50 mg CH$_3$CSNH$_2$ was dissolved in 20 mL of ethanol. Subsequently, the CH$_3$CSNH$_2$ solution was slowly added into the Na$_2$MoO$_4$·2H$_2$O solution, followed by sonication for 30 min. Afterward, the mixture was transferred to the Teflon-lined stainless-steel autoclave (50 mL) and heated at 200 °C for 12 h. The product was rinsed with ethanol and then dried at 60 °C for 12 h.
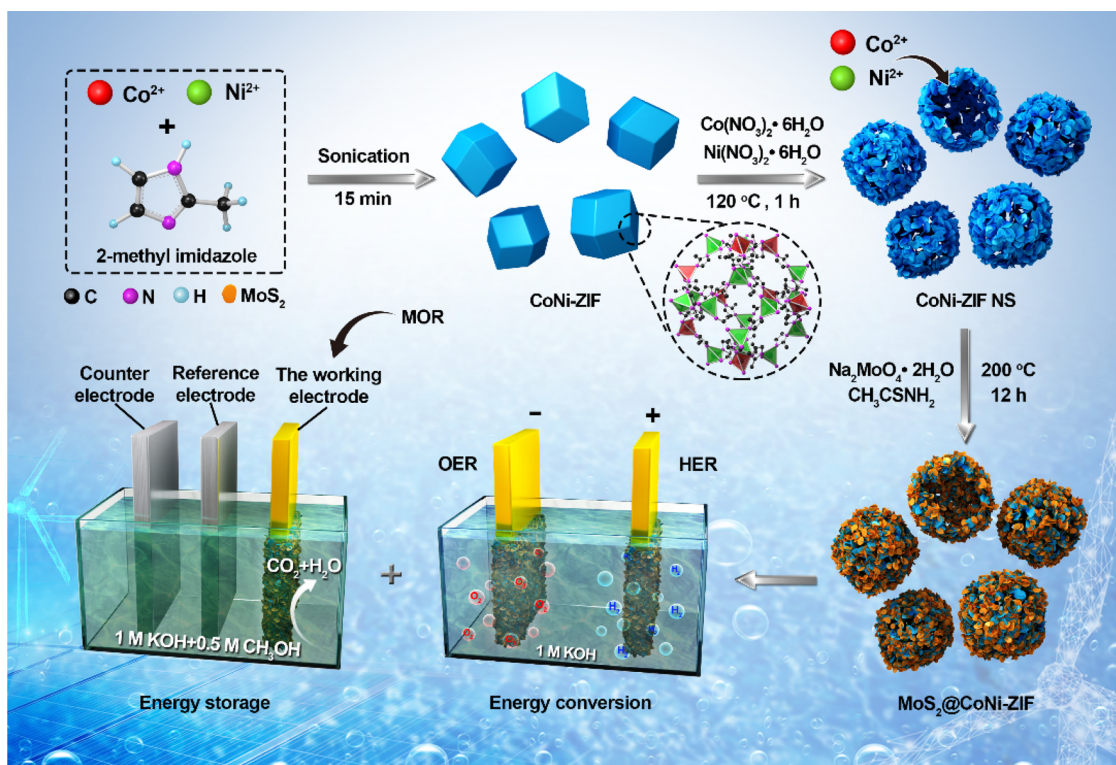
2.3. Preparation of CoNi-ZIF NSs and MoS$_2$@CoNi-ZIF composites

The CoNi-ZIF NSs were synthesized by a modified method according to literature [15]. Briefly, 0.55 g Co(NO$_3$)$_2$·6H$_2$O and 0.55 g Ni(NO$_3$)$_2$·6H$_2$O were dissolved in methanol (30 mL) under magnetic stirring to form the solution **I**. Two copies of the solution **I** were prepared for further use. 1.32 g 2-methyl imidazole was dissolved in methanol (30 mL) under magnetic stirring to afford the solution **II**. Then, the solution **I** was added into the solution **II**, followed by sonication for 15 min. The mixture was washed by methanol, dispersed in methanol (30 mL) and mixed with the solution **I**. Then, the mixture was moved into a Teflon-lined stainless-steel autoclave (100 mL) and heated at 120 °C for 1 h. Finally, the CoNi-ZIF NSs were rinsed with ethanol and dried at 60 °C for overnight.

For the preparation of the series of MoS$_2$@CoNi-ZIF composites, the as-synthesized MoS$_2$ NSs with different dosages were added in the synthetic system of CoNi-ZIF NSs. According to the ratios of MoS$_2$:CoNi-ZIF NSs (*i.e.*, 1:1, 3:1, and 5:1), the composites were represented by MoS$_2$@CoNi-ZIF(1-1), MoS$_2$@CoNi-ZIF(3-1), and MoS$_2$@CoNi-ZIF(5-1), respectively.

2.4. Physicochemical characterizations

X-ray diffraction (XRD) measurement was performed on a Rigaku D/Max-2500 X-ray diffractometer using Cu K_α radiation with the scanning 2θ angle of 5–70°. X-ray photoelectron spectroscopy (XPS) data were measured on a Thermo Fisher ESCALAB 250Xi photoelectron spectrometer equipped with an Al anode (Al-Kα 1486.6 eV). The surface morphologies of all samples were investigated on a JSM-6490LV field emission scanning electron microscope (FE-SEM, Japan) and JEOL JEM-2100 transmission electron microscopy (TEM) with a field emission gun of 200 kV. N$_2$ adsorption and desorption isotherms were collected on a Micromeritics 3Flex surface area and pore size analyzer under ultrahigh vacuum in a clean system.

Scheme 1. Schematic diagram of the preparation of MoS$_2$@CoNi-ZIF catalysts and electrocatalytic performances for MOR and overall water splitting.

2.5. Electrochemical measurements

The catalyst (1.0 mg) was dispersed into 1.0 mL of Milli-Q water to form a homogeneous ink under sonication. Then, 10 µL of the ink was dropped onto the rotating-disk-electrode (RDE) surface (3.0 mm diameter) by a transfer liquid gun and dried naturally. Accordingly, the mass loading of active materials is 0.143 mg cm^{-2}. All electrochemical measurements were taken on a CHI 760E electrochemical workstation equipped with a conventional three-electrode cell with 1.0 M KOH as the electrolyte solution, of which a Pt wire, silver/silver chloride (Ag/AgCl) electrode, and RDE covered with a thin catalyst film were employed as the counter, reference, and working electrodes, respectively. Methanol oxidation measurements were carried out using cyclic voltammetry (CV) with the scan rate of 50 mV s^{-1}, using 0.5 M CH$_3$OH in 1.0 M KOH electrolyte. Electrochemical double-layer capacitance measurements of the working electrode were performed by using CV curves for two cycles between 1.12 and 1.22 V *vs.* RHE with scanning rates of 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mV s^{-1}. The current density differences between the minimum and maximum values at 1.17 V *vs.* RHE and the corresponding scanning rates were used to calculate the EDLC values. All potentials were *iR* corrected and referenced to RHE by the equation: $E_{RHE} = E_{Ag/AgCl} + (0.197 + 0.0591 \times pH)$ V.

The OER or HER activities and overall water splitting were characterized by linear sweep voltammetry (LSV) with the scan rate of 10 mV s^{-1}. RDE and glass carbon electrode (GCE) of 3 mm in diameter were used as the working electrode in OER and HER tests, respectively. In the two-electrode configuration of overall water splitting, MoS$_2$@CoNi-ZIF catalysts were used as both cathode and anode for HER and OER, respectively. Electrochemical impedance spectroscopy (EIS) measurements were taken in the potentiostatic state from 0.01 to 10^5 Hz with a modulation amplitude of 10 mV. Chronopotentiometry tests were implemented at a current density of 10 mA cm^{-2}. Overall water splitting was performed in a two-electrode system where the positive electrode and negative electrode used the same materials.

3. Results and discussion

3.1. Crystal and chemical structures of the series of MoS$_2$@CoNi-ZIF NSs

The crystal structures of the series of MoS$_2$@CoNi-ZIF NSs were characterized by XRD (Fig. 1a). The XRD pattern of MoS$_2$ demonstrates (curve i) four clear diffraction peaks, which are due to the hexagonal structure of MoS$_2$ (JCPDS card no. 77-1716). Additionally, the concomitant appearance of four distinctive diffraction peaks can be detected at 10.2°, 20.1°, 34.0°, and 60.2° for CoNi-ZIF NSs (curve ii) [15]. After MoS$_2$ NSs were coated onto surface of CoNi-ZIF, the diffraction peaks for MoS$_2$@CoNi-ZIF(1-1) (curve iii), MoS$_2$@CoNi-ZIF(3-1) (curve iv), and MoS$_2$@CoNi-ZIF(5-1) (curve v) are different, in which the peak located at 9.2° is attributed to MoS$_2$. Nevertheless, no CoNi-ZIF characterized peak is observed, which is mainly due to the full coverage of the thick MoS$_2$ NSs over CoNi-ZIF NSs. Even the peaks at 38.4° and 55.2° of MoS$_2$ are not observed in CoNi-ZIF@MoS$_2$(1-1) composite, they appear in MoS$_2$@CoNi-ZIF(3-1) and MoS$_2$@CoNi-ZIF(5-1) composites as the amount of MoS$_2$ increases.

The Raman spectra of all samples were taken to evaluate their chemical structures (Fig. 1b). MoS$_2$ NSs illustrate two main peaks at 376 and 406 cm^{-1}, corresponding to the E_{2g}^1 and A_{1g} modes of the hexagonal MoS$_2$ crystal, respectively [27]. The peak located at 1576 cm^{-1} is assigned to the G-band, which is often referred to the "disorder" band, while the peak at 1357 cm^{-1} is assigned to the D-band presented in the sp^2 hybridized carbon materials and derived from the E_{2g} vibrational mode [28]. For the CoNi-ZIF NSs, the bands centered at 473 and 516 cm^{-1} are assigned to Ni−O vibrations in CoNi-ZIF NSs [29]. The weak band at 1046 cm^{-1} is ascribed to the deformation mode of hydroxyl [30]. For MoS$_2$@CoNi-ZIF(1-1) (curve iii), MoS$_2$@CoNi-ZIF(3-1) (curve iv), and MoS$_2$@CoNi-ZIF(5-1) (curve v) NSs, the bands are assigned to MoS$_2$ and CoNi-ZIF NSs, indicating the successful combination of MoS$_2$ and CoNi-ZIF NSs.

Variations in chemical structures and components before and after combination of CoNi-ZIF and MoS$_2$ with different dosages were evaluated by XPS (Fig. S1). The related discussion about the XPS results of
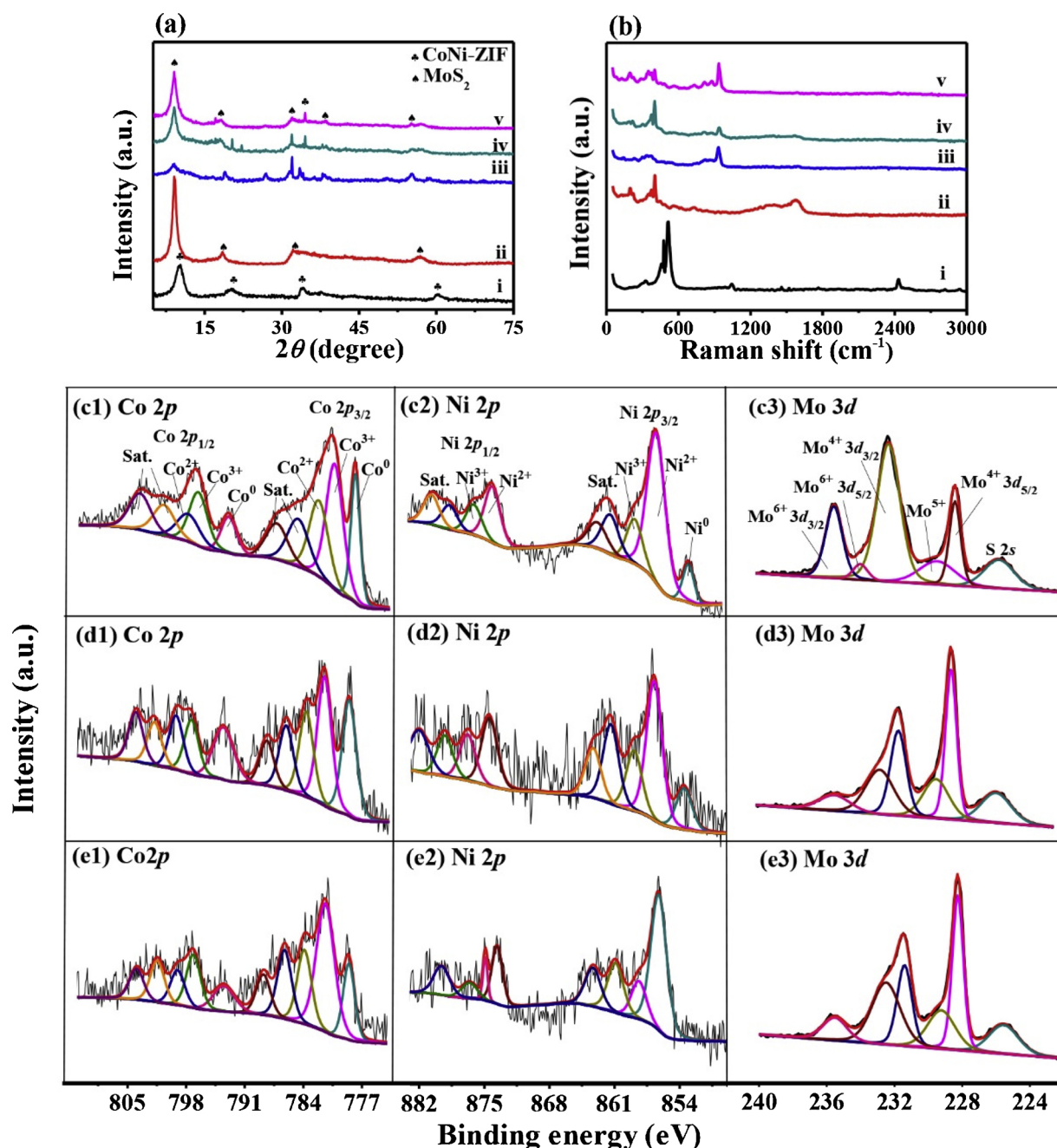
Fig. 1. (a) XRD and (b) Raman spectra of (i) CoNi-ZIF, (ii) MoS_2, (iii) MoS_2@CoNi-ZIF(1-1), (iv) MoS_2@CoNi-ZIF(3-1) and (v) MoS_2@CoNi-ZIF(5-1) NSs. Co 2p, Ni 2p, and Mo 2p core-level XPS spectra of (c) MoS_2@CoNi-ZIF(1-1), (d) MoS_2@CoNi-ZIF(3-1) and (e) MoS_2@CoNi-ZIF(5-1) NSs.

pristine CoNi-ZIF and MoS_2 NSs are given in the part of S1 (Supplementary material). The high-resolution XPS spectra of each element containing in the series of MoS_2@CoNi-ZIF NSs are summarized in Figs. 1c–e and S4. In the high-resolution Co 2p XPS spectra, apart from the characteristic peaks of Co^{2+} and Co^{3+} ions, two peaks at 778.2 and 793.2 eV of the metallic state of Co (Co^0) is observed in all MoS_2@CoNi-ZIF NSs [31]. This indicates that some Co^{2+} ions were reduced to Co^0 during the preparation. Similarly, in addition to Ni^{2+} and Ni^{3+}, the metallic state of Ni (Ni^0) is found at 852.7 eV in the high-resolution XPS spectrum of each sample [32]. The results reveal that Co^{2+} or Ni^{2+} species containing in CoNi-ZIF NSs will be partially reduced to their metallic states when thioacetamide was used. The co-existence of metallic Co and Ni contributes to the improvement of electrochemical activity [33]. The ratios of Co^{2+}/Co^{3+} and Ni^{2+}/Ni^{3+} and the contents of metallic Co and Ni were deduced based on the

relative intensity of each peak (Table S2). It demonstrates that the percentage of metallic states Co and Ni in MoS_2@CoNi-ZIF(3-1) is highest. XPS data further suggest that the prepared MoS_2@CoNi-ZIF composites are composed of Co^{3+} and Ni^{2+}, which can provide enough active sites for electrocatalysis [34]. The analysis of the high-resolution Mo 3d XPS spectra of the series of MoS_2@CoNi-ZIF composites (Fig. 1c3, d3, and e3) reveals a similar result to that of pure MoS_2 (Fig. S2a), indicating its chemical stability. Abundant Mo^{4+} species in MoS_2@CoNi-ZIF composites facilitate the improvement of their electrocatalytic activity [35].

3.2. Surface morphologies of MoS_2@CoNi-ZIF NSs

FE-SEM and TEM were used to explore the surface morphologies of the as-prepared MoS_2, CoNi-ZIF, and series of MoS_2@CoNi-ZIF
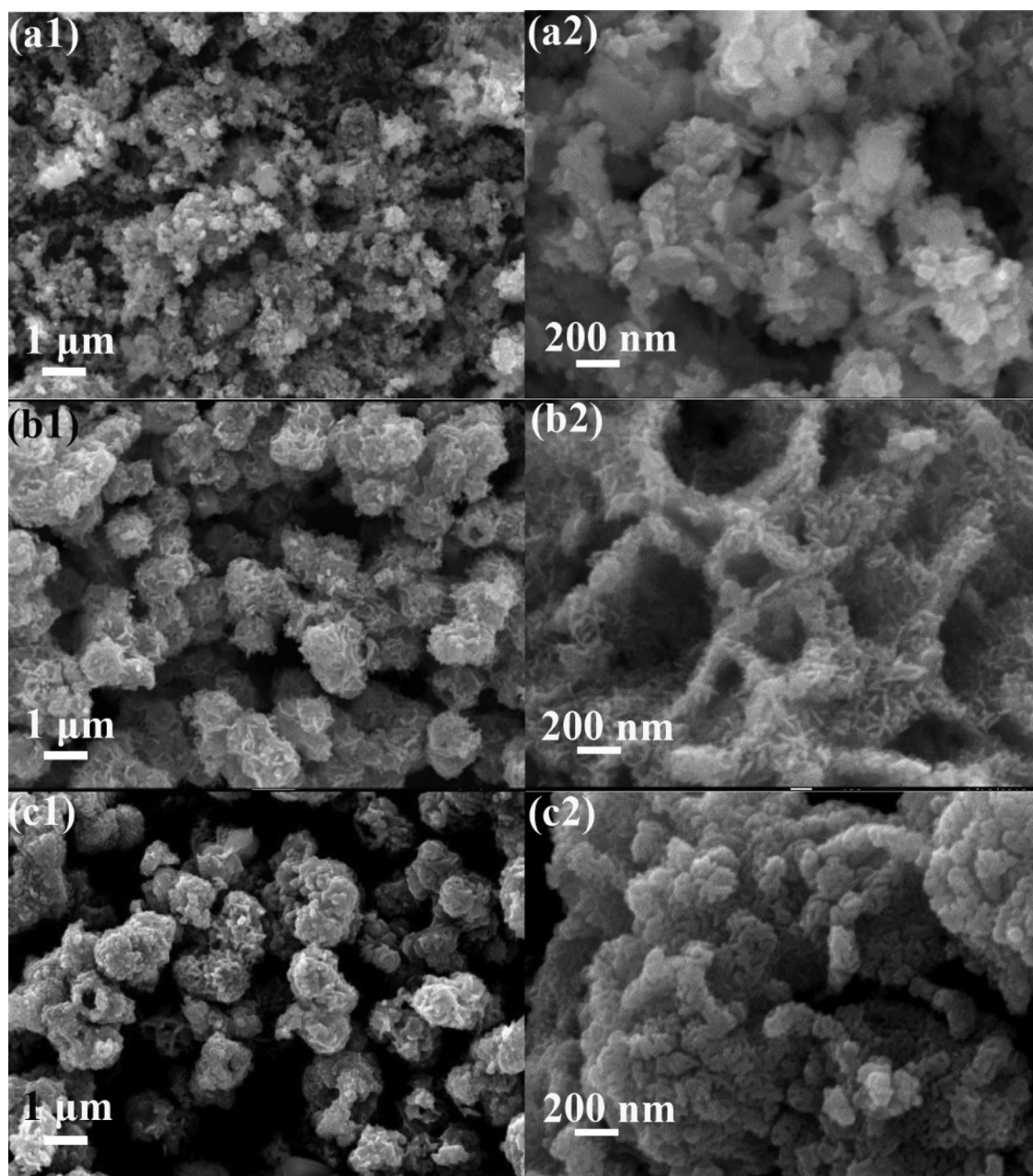
Fig. 2. Low- and high-magnification SEM images of (a1, a2) MoS_2@CoNi-ZIF(1-1), (b1, b2) MoS_2@CoNi-ZIF(3-1), and (c1, c2) MoS_2@CoNi-ZIF(5-1) NSs.

composites. The MoS_2 NSs are aggregated into nanoparticles, while the ultrathin CoNi-ZIF NSs are assembled into hollow nanospheres (S2 in Supplementary material). It seems that the morphology of MoS_2@CoNi-ZIF changes as the amount of MoS_2 increases (Fig. 2). MoS_2@CoNi-ZIF(1-1) composite is composed of NSs with various sizes, thereby accumulating into large blocks (Fig. 2a1 and a2). MoS_2@CoNi-ZIF(3-1) nanocomposite presents a flower-like nanostructure (Fig. 2b1 and b2), while CoNi-ZIF NSs become thick due to the growth of MoS_2 on CoNi-ZIF surface. The original shape of CoNi-ZIF is not maintained in MoS_2@CoNi-ZIF(5-1) composite because the thick MoS_2 layer negatively affects the crystallization behavior of CoNi-ZIF (Fig. 2c1 and c2).

In Fig. 3a1, the TEM image of MoS_2@CoNi-ZIF(1-1) composite shows that MoS_2 NSs grow on surface of CoNi-ZIF, which is further confirmed by high-resolution TEM (HR-TEM) (Fig. 3a2 and a3). The crystal lattice fringe spacing ascribed to the MoS_2 plane is present, whereas the lattice fringe spacings of 0.15 and 0.22 nm are attributed to (220) and (200) planes of CoO (Fig. 3a3), respectively [36]. In

MoS_2@CoNi-ZIF(3-1) composite, the well distributed hollow nanospheres with 400 nm diameter are obtained, which are embedded by MoS_2 NSs. In Fig. 3b3, the lattice fringe spacings of 0.22 and 0.24 nm in HR-TEM image indicate the (200) plane of CoO and (111) plane of NiO, respectively. This observation demonstrates that the MoS_2 layer thickens around MoS_2@CoNi-ZIF(3-1), in which the lattice fringe spacing of CoO or NiO is not easily formed (Fig. 3c2 and c3). The EDS mapping analysis for MoS_2@CoNi-ZIF composites proves the homogeneous distribution of Co, Ni, and Mo (Fig. 4).

The N_2 adsorption-desorption isotherms of MoS_2@CoNi-ZIF composites were explored (Fig. S7a). The CoNi-ZIF, MoS_2@CoNi-ZIF(1-1) and MoS_2@CoNi-ZIF(3-1) exhibit type IV adsorption curves with distinct hysteresis loops in the P/P_0 range of 0.5–1.0, hinting their mesoporous nature that can also be confirmed by the pore size distribution [37]. As shown in Fig. S7b, CoNi-ZIF shows micro/mesoporous characteristic, while MoS_2@CoNi-ZIF composites show mesoporous feature. The specific surface area of CoNi-ZIF is estimated to be 95.7 $m^2\,g^{-1}$,
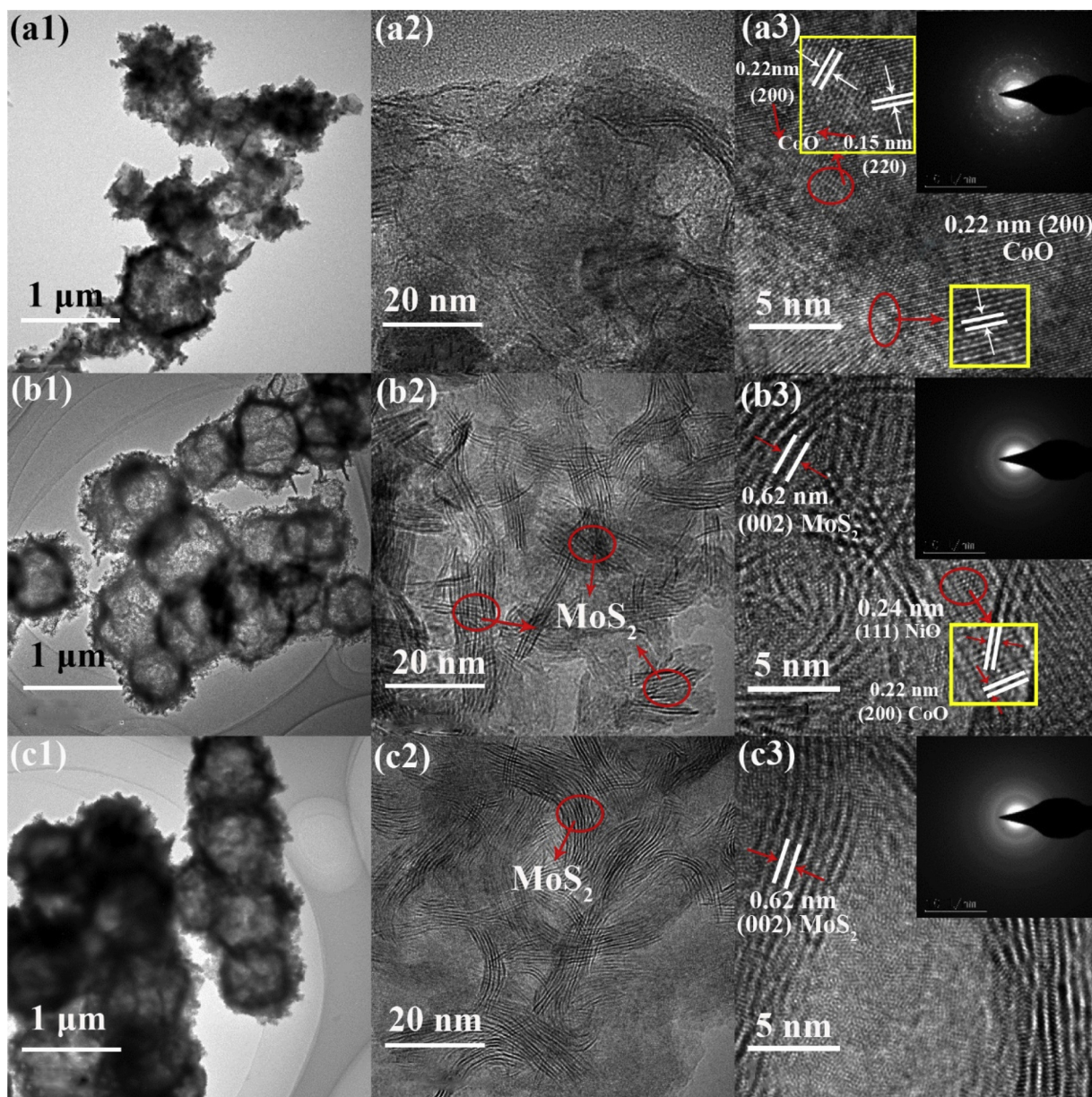
Fig. 3. TEM and HR-TEM images of (a1, a2, a3) MoS$_2$@CoNi-ZIF(1-1), (b1, b2, b3) MoS$_2$@CoNi-ZIF(3-1), and (c1, c2, c3) MoS$_2$@CoNi-ZIF(5-1) NSs (the insets of a3, b3, and c3: their corresponding SEAD patterns).

whereas that of MoS$_2$ NSs is only 7.83 m^2 g^{-1}. As such, the combination of CoNi-ZIF and MoS$_2$ results in the decrease of specific surface areas for MoS$_2$@CoNi-ZIF composites, which are evaluated to be 46.1, 33.8, and 9.6 m^2 g^{-1}, for MoS$_2$@CoNi-ZIF(1-1), MoS$_2$@CoNi-ZIF(3-1), and MoS$_2$@CoNi-ZIF(5-1), respectively. The mesoporous void is helpful for the efficient mass transport in the electrocatalytic reaction, but this is not the sole factor that affects the catalytic activity [38].

3.3. Electrochemical MOR performances of MoS$_2$@CoNi-ZIF in the alkaline solution

Considering the excellent MOR performances of both MoS$_2$- and CoNi-related materials, MOR properties of the series of MoS$_2$@CoNi-ZIF composites were studied. The CV curves of MoS$_2$, CoNi-ZIF, and MoS$_2$@CoNi-ZIF composites were measured in 1.0 M KOH solution at the scan rate of 50 mV s^{-1} (Fig. 5a). No obvious redox peak is found in CV curve of MoS$_2$-modified electrode, suggesting its poor electrochemical activity. For MoS$_2$@CoNi-ZIF composites, the CV curves are nonrectangular, indicating the reversible redox reactions. Notably, the MoS$_2$@CoNi-ZIF(3-1)-modified electrode shows a pair of well-defined redox peaks consisting of an anodic peak at 0.42 V and a cathodic peak at 0.26 V. These peaks are attributed to the oxidation of Co^{2+} and reduction of Ni^{3+}. Previous research reveals that Co^0, Co^{2+}, and Co^{3+} can undergo electrochemical charge transfer reactions of Co$^0 \leftrightarrow$ Co^{2+} $\leftrightarrow$ Co^{3+} $\leftrightarrow$ Co^{4+} in alkaline solutions [39]. The redox process of Ni^0/Ni^{2+}/Ni^{3+} can also occur [40]. In this case, the peaks caused by each redox couple are not distinct, and only one pair of redox peaks situated at 0.26 V/0.42 V (*vs.* RHE) is clearly observed. This may be because the electrochemical reactions of Co^{2+}/Co^{3+} and Ni^{2+}/Ni^{3+} simultaneously occur, resulting in the overlap of redox peaks. Among the CV curves of the three MoS$_2$@CoNi-ZIF composites, the MoS$_2$@CoNi-ZIF(3-1)-modified electrode shows the highest peak current density and the largest enclosed area, indicating that the redox current density of this electrode is superior to that of other MoS$_2$@CoNi-ZIF-based electrodes. The contents of the metallic state Co/Ni and the ratios of Co^{2+}/Co^{3+} and Ni^{3+}/Ni^{2+} in the MoS$_2$@CoNi-ZIF(3-1) catalyst are the highest,
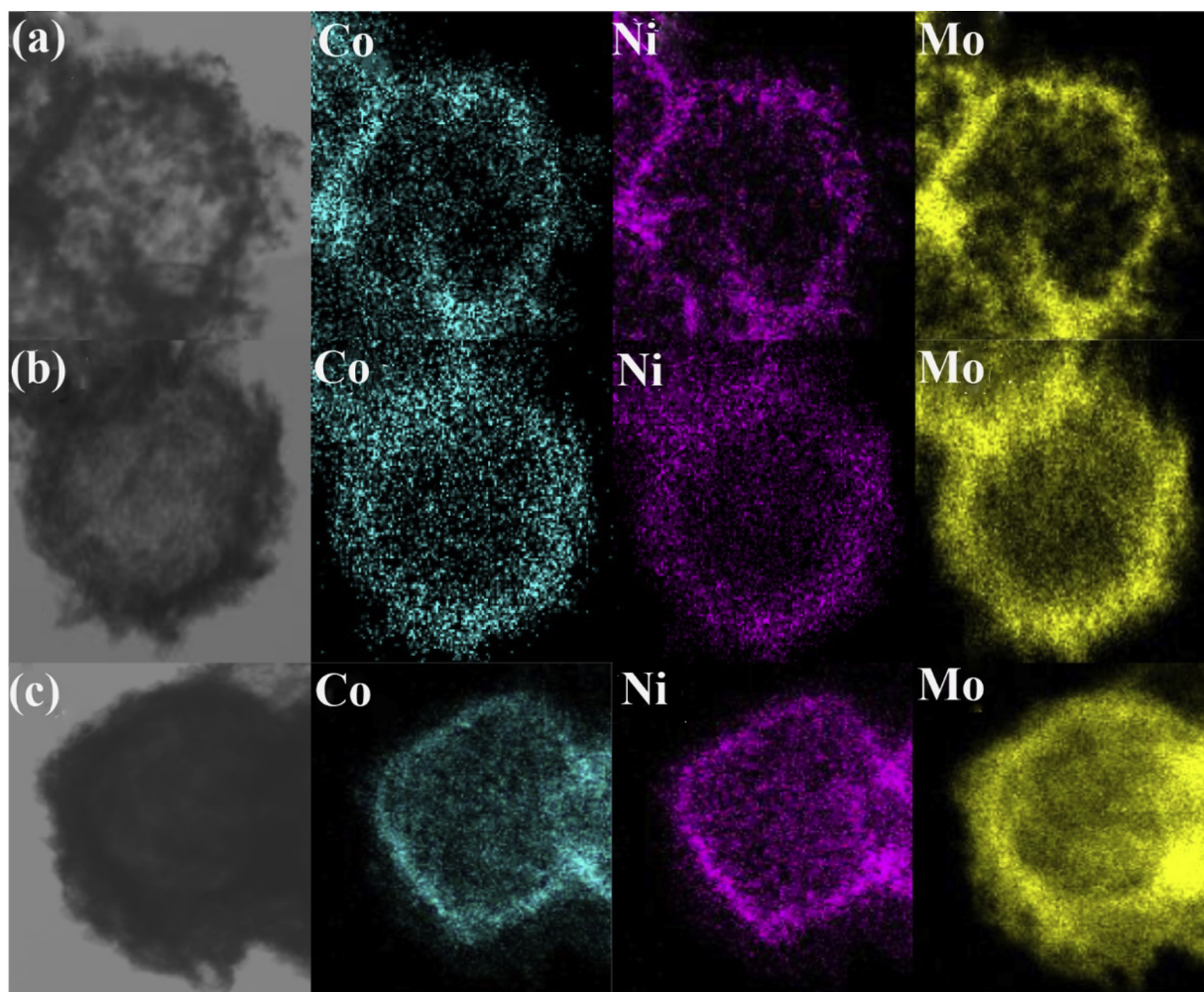
Fig. 4. Elemental mapping of homogenously distributed Co (cyan), Ni (purple), and Mo (yellow) containing in the series of (a) MoS$_2$@CoNi-ZIF(1-1), (b) MoS$_2$@CoNi-ZIF(3-1), and (c) MoS$_2$@CoNi-ZIF(5-1) NSs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

suggesting the superior electrocatalytic activity of this catalyst.

The MOR activities of MoS$_2$, CoNi-ZIF and MoS$_2$@CoNi-ZIF composites were examined by adding the mixed solution of 1.0 M KOH and 0.5 M CH$_3$OH (Fig. 4b). The results show the electro-oxidation reactions of CH$_3$OH on the electrodes modified by these materials except for MoS$_2$. The anodic currents of methanol oxidation for all MoS$_2$@CoNi-ZIF catalysts sharply increase. The maximum current densities of methanol oxidation for MoS$_2$, CoNi-ZIF, MoS$_2$@CoNi-ZIF(1-1), MoS$_2$@CoNi-ZIF(3-1), and MoS$_2$@CoNi-ZIF(5-1) catalysts at 0.6 V are 27.65, 86.24, 191.38, 430.08, and 229.32 mA g^{-1}, respectively. In addition, onset potential is a critical parameter for evaluating the MOR catalytic performance. Fig. 5b shows that the onset potentials of MoS$_2$, CoNi-ZIF, MoS$_2$@CoNi-ZIF(1-1), MoS$_2$@CoNi-ZIF(3-1), and MoS$_2$@CoNi-ZIF(5-1) are 1.43, 1.31, 1.26, 1.24, and 1.3 V, respectively. That is to say, the catalytic activity of MoS$_2$@CoNi-ZIF(3-1)-based electrode outperforms the electrodes based on other materials. The obtained onset potential of MoS$_2$@CoNi-ZIF(3-1)-based electrode is smaller than that reported in previous studies of metal oxide-based electrocatalysts for MOR [41]. Fig. S8 illustrates that the CV curve of MoS$_2$@CoNi-ZIF(3-1) measured in 1.0 M KOH is quite different from that measured in the mixed solution of KOH and CH$_3$OH. The onset potential of MoS$_2$@CoNi-ZIF(3-1) catalyst of MOR is around 0.1 V, and even the individual CoNi-ZIF and MoS$_2$ catalysts exhibit poor electrochemical activity. Their integration can enhance the electro-oxidation ability, indicating that the as-prepared MoS$_2$@CoNi-ZIF(3-1)-modified

electrode can be used as an efficient MOR catalyst in alkaline solution. Herein, all potentials were converted to the ones of RHE for an equal comparison, and the synergistic electrocatalytic activity of the MoS$_2$@CoNi-ZIF(3-1) electrode in MOR was assessed by comparing the mass activities with other catalysts (Fig. 5b inset). The mass activity of MoS$_2$@CoNi-ZIF(3-1) is 430.08 mA g^{-1}, which is 2.25, 1.88, 4.99, and 15.56 times higher than those of MoS$_2$@CoNi-ZIF(1-1) (191.38 mA g^{-1}), MoS$_2$@CoNi-ZIF(5-1) (229.32 mA g^{-1}), CoNi-ZIF (86.24 mA g^{-1}), and MoS$_2$ (27.65 mA g^{-1}), respectively.

In Fig. 5c, the CVs recorded in CH$_3$OH solution with different concentrations from 0.2 to 0.7 M reveal the influence of CH$_3$OH concentration on MOR electrocatalytic activity of the MoS$_2$@CoNi-ZIF(3-1)-modified electrode, showing that the anodic peak current increases with the increase of CH$_3$OH concentration. This reveals a typical electrocatalytic response of MOR. Additionally, the maximum current density is proportional to CH$_3$OH concentration (Fig. 5c inset). The CV curve was also measured on the MoS$_2$@CoNi-ZIF(3-1)-modified electrode with the scan rate increasing from 20 to 300 mV s^{-1}, but no obvious change in the shape of CV curves is found due to the fast reaction kinetics, which originates from the porous structure and fast electron transfer of electroactive materials [42]. The linear relationship obtained from the methanol oxidation peak current and the square root of scan rate reveals a diffusion-controlled process of the electrocatalytic reaction [43]. Oxidation potential and methanol oxidation current are essential parameters for performance assessment of MOR catalysts.
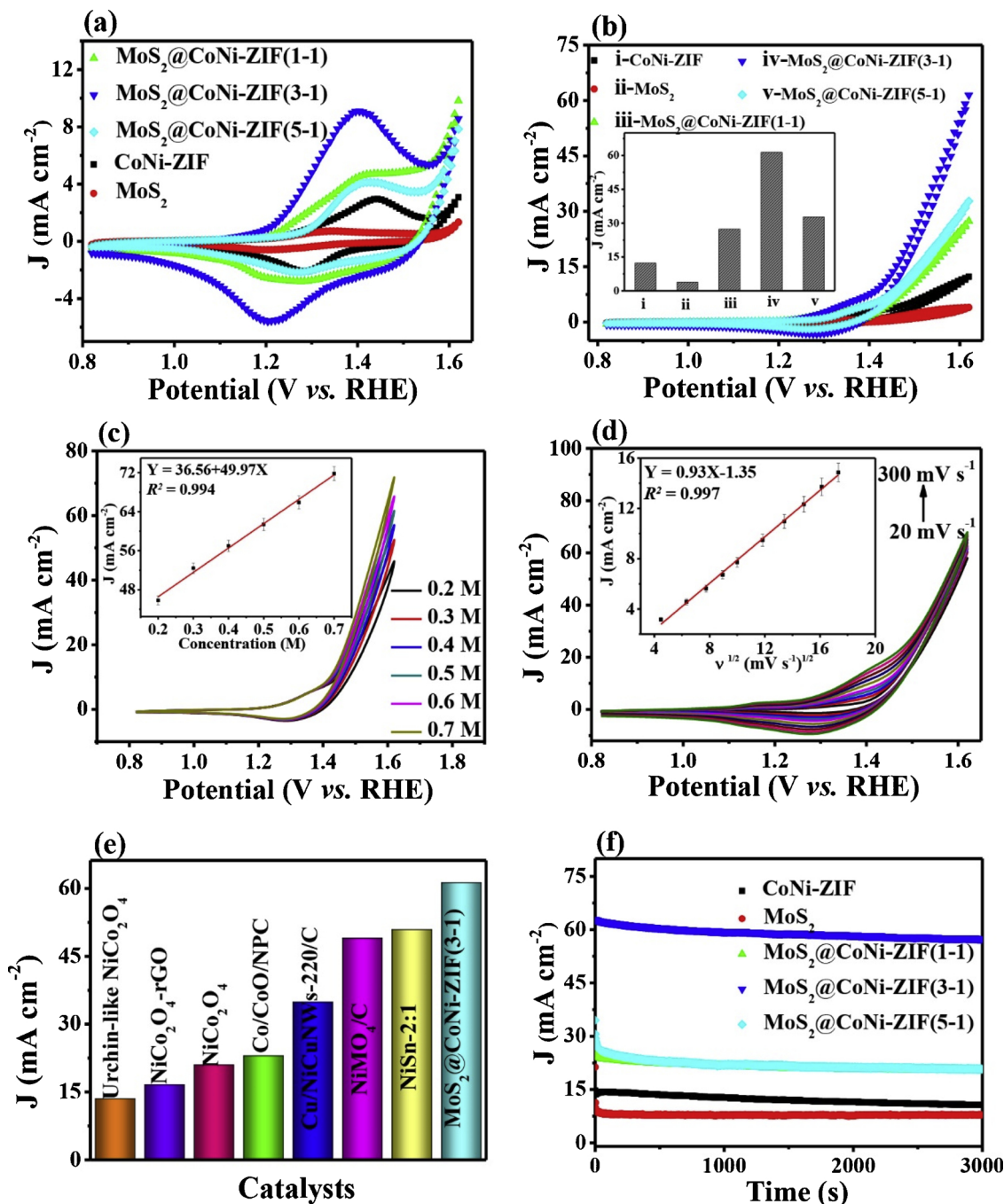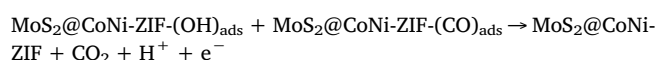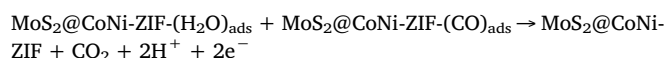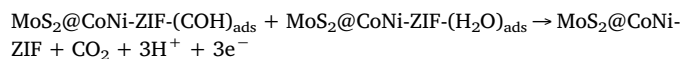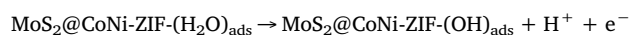
Fig. 5. (a) CVs of CoNi-ZIF, MoS₂, MoS₂@CoNi-ZIF(1-1), MoS₂@CoNi-ZIF(3-1), and MoS₂@CoNi-ZIF(5-1) recorded in 1.0 M KOH solution and (b) 1.0 M KOH + 0.5 M CH₃OH at the scan rate of 50 mVs⁻¹. (c) CV curves of MoS₂@CoNi-ZIF(3-1) in the CH₃OH solution with different concentrations (inset: the relationship between the peak oxidation current at 1.6 V and concentration of CH₃OH for MoS₂@CoNi-ZIF(3-1)). (d) CV curves of MoS₂@CoNi-ZIF(3-1) electrode in 1.0 M KOH solution at different scan rates (inset: the relationship of the anodic peak currents *vs* scan rates of MoS₂@CoNi-ZIF(3-1) electrode). (e) Comparison of the reported catalysts of the current density. (f) Chronoamperometric curves of MoS₂@CoNi-ZIF(3-1) recorded in 1.0 M KOH + 0.5 M CH₃OH solution at 1.6 V potential before and after 3000 cycles between 0.8 and 1.6 V *vs.* RHE.

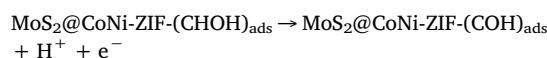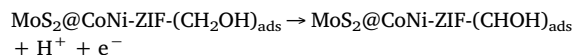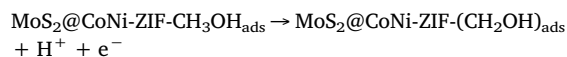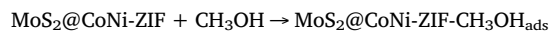Compared with other state-of-the-art Co- or Ni-based catalysts (Table S3 and Fig. 5e), MoS₂@CoNi-ZIF(3-1) exhibits a superior electro-catalytic activity, as confirmed by both high peak current density and low peak potential. Fig. 5f shows the chronoamperograms recorded for 3000 s in mixed solution of 1.0 M KOH and 0.5 M CH₃OH. The potential was held at the oxidation peak potential during measurements. The current density sharply decreases at the beginning and then slightly decreases for poisoning of catalysts. Among them, the degradation rate of MoS₂@CoNi-ZIF(3-1) is obviously less than those of other catalysts, revealing its excellent durability. Regarding to the dual pathway

mechanism of methanol oxidation, the intermediate species generated in the indirect pathway can be strongly immobilized on the catalyst surface to occupy the reaction active sites. It further results in a serious decrease in reaction kinetics and is responsible for the poisoning of catalytic sites [44]. The CV curve of MoS₂@CoNi-ZIF(3-1) in MOR remains stable after 3000 cycles (Fig. S8b), indicating its good stability.

The Nyquist plots of all materials were investigated to explore the catalytic mechanism of MoS₂@CoNi-ZIF(3-1) in MOR (Fig. S9), and the experimental data were simulated by an equivalent circuit model (Fig. S9 inset). The simulated equivalent circuit consists of charge transfer

resistance (R_{ct}), solution resistance (R_s), constant-phase element (CPE), and Warburg impedance (W_o). A small R_{ct} value indicates the quick electron transfer on electrode surface [45]. Therefore, the smallest R_{ct} value of the MoS$_2$@CoNi-ZIF(3-1) electrode (32 Ω) expresses the greatest electro-catalytic kinetics behavior of electro-oxidation. Accordingly to the basic characterizations and electrochemical behaviors, the electrocatalytic activity and stability of MoS$_2$@CoNi-ZIF could be attributed to the following factors: (i) a low onset potential and a quick electrode kinetics are the inherent factors that notably enhance the MOR activity; (ii) the architecture with functional mesopores, epitaxial MoS$_2$ orientation and hierarchical voids facilitate the electron diffusion to active centers [46]; (iii) rich Ni^{2+}, Co^{3+}, and Mo^{4+} active sites can efficiently strengthen the reaction kinetics, resulting in a remarkable electrocatalytic MOR performance [47,48]; and (iv) the synergistic effect of CoNi-ZIF and MoS$_2$ leads to the MOR activity enhancement of the catalyst. In general, the combined effect of these factors will greatly improve both catalytic activity and stability of MoS$_2$@CoNi-ZIF catalyst. Additionally, the overall process of MOR undergoes some necessary elementary steps, such as adsorption of methanol, dehydrogenation of methanol into intermediates, and oxidation of these intermediates into CO$_2$ [49]. When the MOR takes places, methanol is adsorbed on the MoS$_2$@CoNi-ZIF surface as well as CoNi-ZIF and MoS$_2$, providing more surface areas and edge sites for methanol adsorption and decomposition into the hydroxide and hydrogen ions [20,50]. The pores of MOFs also adsorb hydroxide ions that can enhance the oxidation of the adsorbed CO and thus regenerate the active sites of catalysts [51]. Consequently, the synergic effect between CoNi-ZIF and MoS$_2$ increases hydroxide adsorption and improves catalytic activity and stability. The electron transfer mechanism of MoS$_2$@CoNi-ZIF(3-1) catalyst surface in alkaline media in MOR possibly obeys the following steps:

$$MoS_2@CoNi\text{-}ZIF + CH_3OH \rightarrow MoS_2@CoNi\text{-}ZIF\text{-}CH_3OH_{ads}$$

$$MoS_2@CoNi\text{-}ZIF\text{-}CH_3OH_{ads} \rightarrow MoS_2@CoNi\text{-}ZIF\text{-}(CH_2OH)_{ads} + H^+ + e^-$$

$$MoS_2@CoNi\text{-}ZIF\text{-}(CH_2OH)_{ads} \rightarrow MoS_2@CoNi\text{-}ZIF\text{-}(CHOH)_{ads} + H^+ + e^-$$

$$MoS_2@CoNi\text{-}ZIF\text{-}(CHOH)_{ads} \rightarrow MoS_2@CoNi\text{-}ZIF\text{-}(COH)_{ads} + H^+ + e^-$$

$$MoS_2@CoNi\text{-}ZIF\text{-}(COH)_{ads} \rightarrow MoS_2@CoNi\text{-}ZIF\text{-}(CO)_{ads} + H^+ + e^-$$

$$MoS_2@CoNi\text{-}ZIF + H_2O \rightarrow MoS_2@CoNi\text{-}ZIF\text{-}(H_2O)_{ads}$$

$$MoS_2@CoNi\text{-}ZIF\text{-}(H_2O)_{ads} \rightarrow MoS_2@CoNi\text{-}ZIF\text{-}(OH)_{ads} + H^+ + e^-$$

$$MoS_2@CoNi\text{-}ZIF\text{-}(COH)_{ads} + MoS_2@CoNi\text{-}ZIF\text{-}(H_2O)_{ads} \rightarrow MoS_2@CoNi\text{-}ZIF + CO_2 + 3H^+ + 3e^-$$

$$MoS_2@CoNi\text{-}ZIF\text{-}(H_2O)_{ads} + MoS_2@CoNi\text{-}ZIF\text{-}(CO)_{ads} \rightarrow MoS_2@CoNi\text{-}ZIF + CO_2 + 2H^+ + 2e^-$$

$$MoS_2@CoNi\text{-}ZIF\text{-}(OH)_{ads} + MoS_2@CoNi\text{-}ZIF\text{-}(CO)_{ads} \rightarrow MoS_2@CoNi\text{-}ZIF + CO_2 + H^+ + e^-$$

3.4. HER performances in basic solution

Considering the excellent HER properties of MoS$_2$ and good OER activity of CoNi-MOF [52], the HER and OER performances of MoS$_2$@CoNi-ZIF in alkaline solution was investigated (Figs. 6 and 7). The MoS$_2$@CoNi-ZIF composite (0.14 mg cm^{-2}) was directly used as an integrated electrode to catalyze HER under alkaline condition in a three-electrode configuration. Fig. 6a depicts the corrected linear sweep voltammetry (LSV) curves of MoS$_2$@CoNi-ZIF electrodes obtained at 10 mV s^{-1} on the RHE scale in 1.0 M KOH solution. For comparison, the LSV curves of MoS$_2$, CoNi-ZIF and commercial Pt/C (20%) catalysts

were obtained under the same condition. As expected, the commercial Pt/C (20%) requires a low overpotential of 80 mV at 10 mA cm^{-2} (η_{10}) and an onset potential of 10 mV (η_0). However, the CoNi-ZIF catalyst requires a large overpotential of 490 mV to drive HER at a current density of 10 mA cm^{-2}, while the overpotential of MoS$_2$ is 420 mV. Among three kinds of CoNi-ZIF@MoS$_2$ composites, MoS$_2$@CoNi-ZIF(3-1) yields a small η_0 of 50 mV and η_{10} of 153 mV, which are smaller than those of two other composites, namely, MoS$_2$@CoNi-ZIF(1-1) (η_0 = 110 mV and η_{10} = 220 mV) and MoS$_2$@CoNi-ZIF(5-1) (η_0 = 90 mV and η_{10} = 220 mV) (Table S4). This indicates that the electrocatalytic performance of MoS$_2$@CoNi-ZIF(3-1) toward HER is superior to those of other HER catalysts (Table S5 and Fig. 6b).

The linear portions of Tafel plots of all catalysts were fitted to the Tafel equation (η = a + blog$j$), in which j is the current density and b is the Tafel slope (Fig. 6c and Table S4). The results show that MoS$_2$@CoNi-ZIF(3-1) delivers a Tafel slope of 68 mV dec^{-1} that is close to Pt/C (65 mV dec^{-1}) [53], suggesting that the HER is consistent with the Volmer-Heyrovsky mechanism. The Tafel slopes for MoS$_2$@CoNi-ZIF(1-1) and MoS$_2$@CoNi-ZIF(5-1) are also smaller than those of CoNi-ZIF (218 mV dec^{-1}) and MoS$_2$ (168 mV dec^{-1}). Considering that the Tafel slope is directly associated with the reaction kinetics of electrocatalysts, it is speculated that the lower Tafel slope of MoS$_2$@CoNi-ZIF (3-1) implies a faster catalytic kinetics and a higher catalytic activity of HER than other materials. Thus, the combination of CoNi-ZIF and MoS$_2$ can enhance electrocatalytic activity *via* a strong synergistic effect between MoS$_2$ and CoNi-ZIF.

Durability and stability are vital criteria to assess a catalyst [4]. The stability of MoS$_2$@CoNi-ZIF(3-1) was first determined by conducting LSV with a potential range of −0.4 to −0.1 V (*vs*. RHE) at a scan rate of 100 mV s^{-1} in 1.0 M KOH (Fig. 6d inset). The MoS$_2$@CoNi-ZIF(3-1) electrode exhibits an increase in the overpotential of 3 mV after 5000 LSV cycles to obtain a current density of 10 mA cm^{-2}. The HER long-term durability of MoS$_2$@CoNi-ZIF(3-1) was investigated through electrolysis at a fixed overpotential of 67 mV. Consequently, the cathodic current density remains consistent for 48 h of electrolysis (97.5% of the initial value, Fig. 6d), revealing the outstanding stability of MoS$_2$@CoNi-ZIF(3-1) during HER. Howbeit, the catholic current density of the Pt/C catalyst is only 71.6% of its initial value under the same condition. This is probably attributed to the compositional and structural stability of MoS$_2$@CoNi-ZIF(3-1). Further, to understand the effect of Pt wire as a counter electrode on the test results, long-term durability of MoS$_2$@CoNi-ZIF(3-1) with chronoamperometry test using graphite rod as the counter electrode was measured and the catalyst was characterized by XRD and SEM after stability test. As shown in Fig. S10a, the current density remains 95.2% of the initial value after 48 h. The diffraction peaks of MoS$_2$ can be clearly observed (Fig. S10b). Besides, SEM image after 48 h of durability test shows that the MoS$_2$@CoNi-ZIF(3-1) structure remains similar to the original material (flower-like nanostructure). The results further confirm the excellent stability of MoS$_2$@CoNi-ZIF(3-1) during electrocatalysis.

The kinetic was tested by EIS at an overpotential of 150 mV in 1.0 M KOH (Fig. 6e). R_{ct} is related to the electrocatalytic kinetics at the electrocatalyst/electrolyte interface and a small value corresponds to a fast electron transfer capacity. The EIS spectra display that R_{ct} for MoS$_2$@CoNi-ZIF(3-1) is 42.9 Ω, which is much smaller than those of MoS$_2$@CoNi-ZIF(1-1), MoS$_2$@CoNi-ZIF(5-1), CoNi-ZIF, and MoS$_2$ (84, 57.5, 146, and 168 Ω, respectively), confirming that MoS$_2$@CoNi-ZIF(3-1) possesses a fast electron transfer and favorable HER kinetics at the electrocatalyst/electrolyte interface. Compared to the results in 1.0 M KOH containing 0.5 M CH$_3$OH (Fig. S10), the R_{ct} values for all samples are slightly larger in 1.0 M KOH solution, which has been reported in other literature [54]. Electrochemically active surface area (ECSA) of each catalyst was also investigated and compared to enhance the understanding of their HER performance trend and intrinsic activity. Typically, the double-layer capacitance (C_{dl}) is linearly proportional to ECSA, which can be investigated by measuring CV curves at different
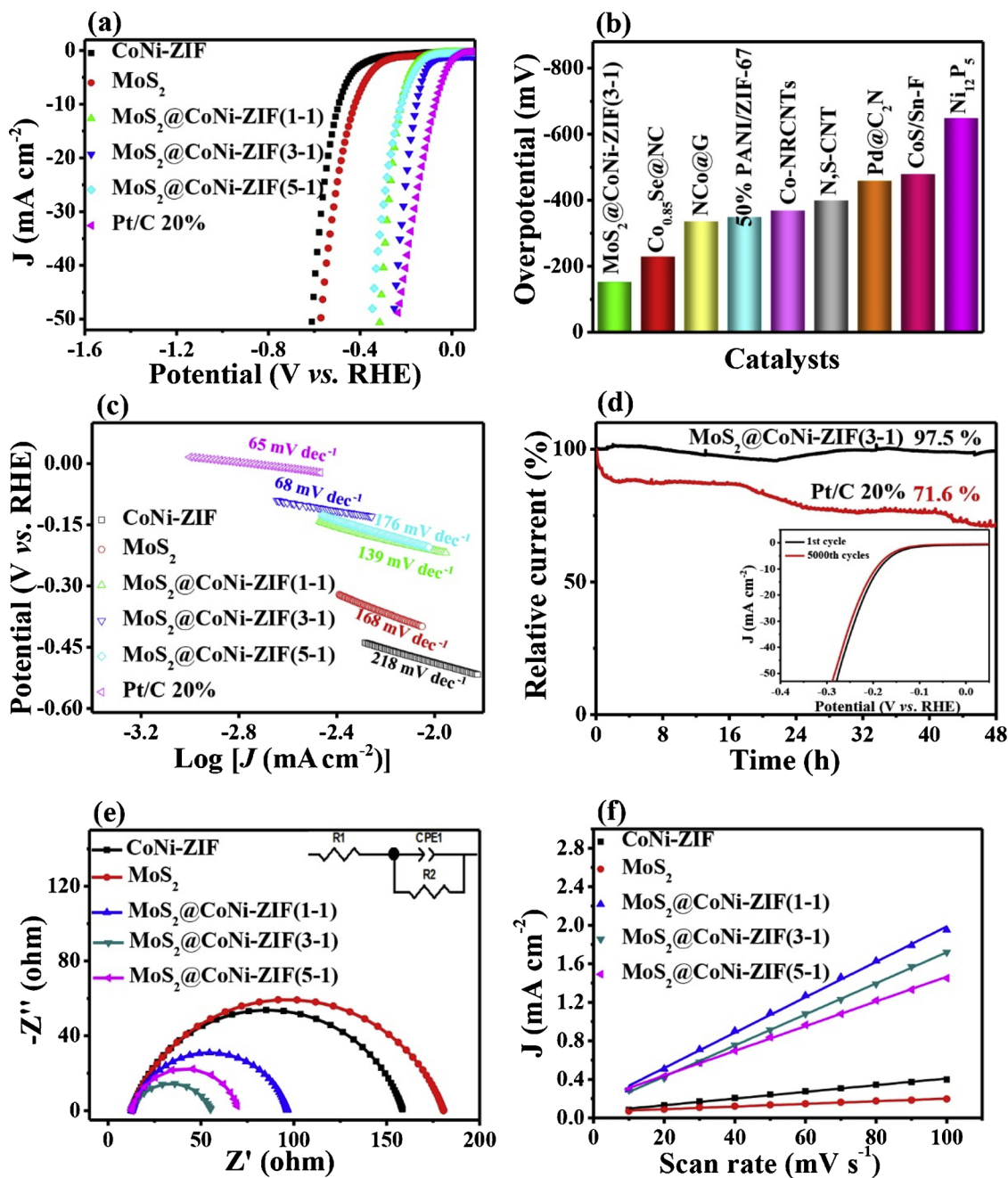
Fig. 6. Electrochemical HER measurements. (a) Linear sweep curves in 1.0 M KOH solution of CoNi-ZIF, MoS$_2$, MoS$_2$@CoNi-ZIF(1-1), MoS$_2$@CoNi-ZIF(3-1), MoS$_2$@CoNi-ZIF(5-1) and Pt/C (20%). (b) Comparison of the known catalysts of the overpotential at 10 mA cm^{-2}. (c) The corresponding Tafel plots of (a). (d) The *I–t* responses for MoS$_2$@CoNi-ZIF(3-1) and Pt/C at a constant η_{10} of 120 mV (*vs.* RHE) for 48 h in N$_2$-saturated 1.0 M KOH solution (inset: polarization curves of MoS$_2$@CoNi-ZIF(3-1) before and after 5000 cycles with scan rate of 10 mV s^{-1} between 0.1 and −0.8 V *vs.* RHE). (e) EIS curves and (f) plots of capacitive currents density (j_{anodic} − $j_{cathodic}$) of CoNi-ZIF, MoS$_2$, MoS$_2$@CoNi-ZIF(1-1), MoS$_2$@CoNi-ZIF(3-1), MoS$_2$@CoNi-ZIF(5-1) catalysts at 0.15 V *vs* Ag/AgCl as a function of various scan rates in 1.0 M KOH solution.

scan rates in a nonfaradaic region of 0.1–0.2 V *vs.* RHE (Fig. S11) [4]. The halves of the differences between positive and negative current densities at the center of the scanning potential ranges are plotted against the scan rates (Fig. 6f) [4]. The calculated C_{dl} of MoS$_2$@CoNi-ZIF(3-1) is 18 mF cm^{-2}, which is much higher than those of MoS$_2$@CoNi-ZIF(1-1) (16 mF cm^{-2}), MoS$_2$@CoNi-ZIF(5-1) (12 mF cm^{-2}), CoNi-ZIF (3.0 mF cm^{-2}), and MoS$_2$ (1.0 mF cm^{-2}). These results confirm that MoS$_2$@CoNi-ZIF(3-1) has more effective active sites at the solid-liquid interface, resulting in a higher electrochemical activity for HER.

3.5. OER performances in basic solution

Electrocatalytic activities of composites for OER in alkaline solution were also systematically investigated. The homogeneous dispersion of catalyst was dropped on GCE at a constant loading density of 0.14 mg cm^{-2} across the samples to maintain a consistent comparison. Electrochemical measurements were taken in 1.0 M O$_2$-saturated KOH by using a standard three-electrode system with Ag/AgCl (3.0 M KCl) as a reference electrode and Pt wire as a counter electrode. Fig. 7a shows the corrected LSV curves scanned initially in the anodic direction. All samples exhibit larger current density (*j*). MoS$_2$@CoNi-ZIF(1-1) and
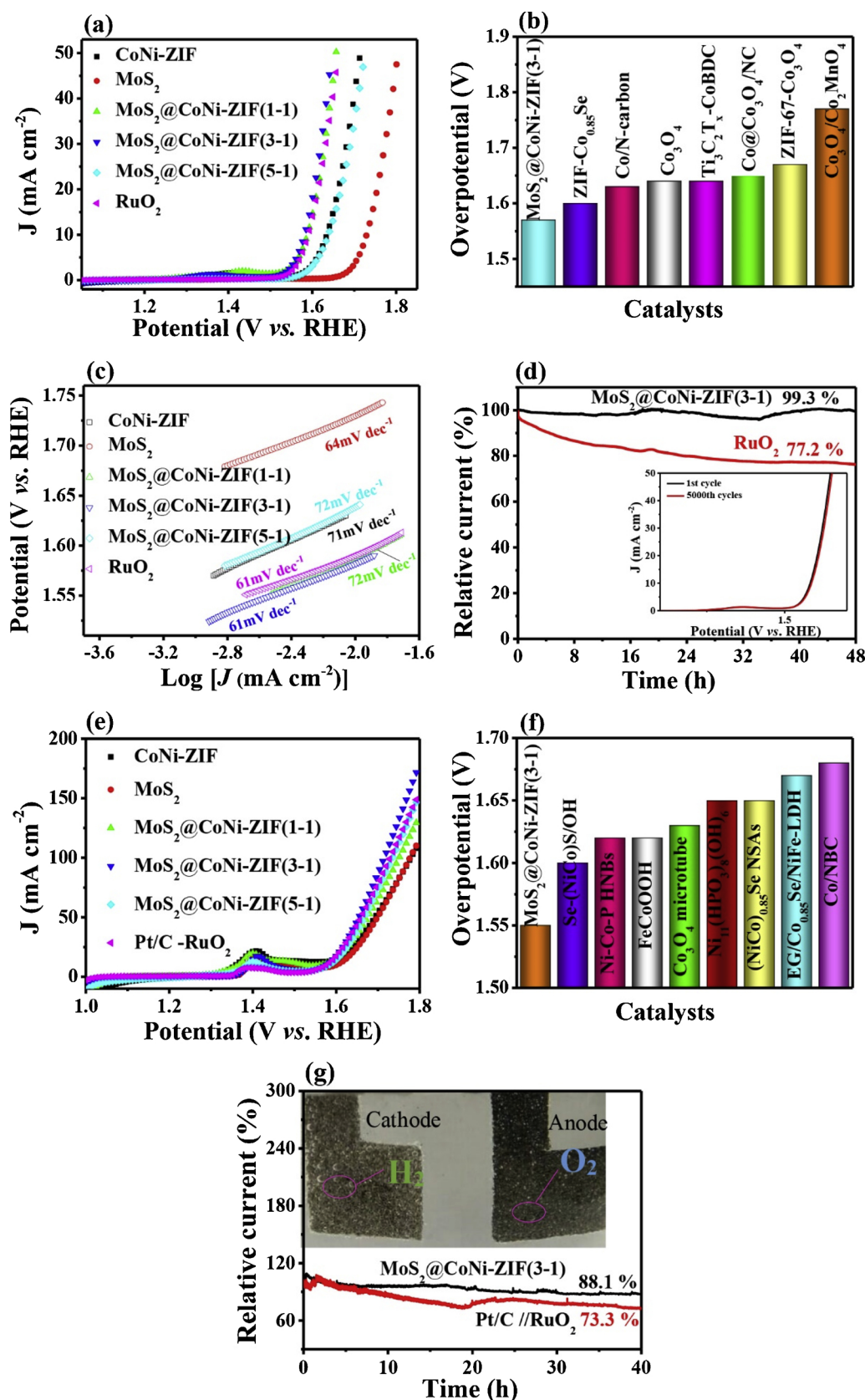
Fig. 7. OER performances of catalysts. (a) Polarization curves of CoNi-ZIF, MoS₂, MoS₂@CoNi-ZIF(1-1), MoS₂@CoNi-ZIF(3-1), MoS₂@CoNi-ZIF(5-1), and RuO₂ (1.0 M KOH, scan rate = 10 mV s⁻¹). (b) Comparison with the known catalysts of the overpotential at 10 mA cm⁻². (c) The corresponding Tafel plots of (a). (d) The *I–t* responses for MoS₂@CoNi-ZIF(3-1) and Pt/C at a constant η₁₀ = 1.57 V (*vs.* RHE) for 48 h in N₂-saturated 1.0 M KOH solution (inset: polarization curves of MoS₂@CoNi-ZIF(3-1) before and after 5000 cycles with the scan rate of 10 mV s⁻¹ between 1.0 and 1.6 V *vs.* RHE). (e) Polarization curves of CoNi-ZIF, MoS₂, MoS₂@CoNi-ZIF(1-1), MoS₂@CoNi-ZIF(3-1), and MoS₂@CoNi-ZIF(5-1) composites in the two-electrode electrolyzers at the scan rate of 10 mV s⁻¹. (f) Comparison of the reported catalysts of the overpotential at 10 mA cm⁻² in a two electrode electrolyzer. (g) Long-term durability test of MoS₂@CoNi-ZIF(3-1) electrolyzer at 10 mA cm⁻² and (inset) the photograph during the overall water splitting.

MoS₂@CoNi-ZIF(3-1) display the earlier onset potential of the catalytic current density, being close to RuO₂. The overpotential required for achieving a current density of 10 mA cm⁻² should be compared [4]. The MoS₂@CoNi-ZIF(3-1) catalyst achieves a small η₁₀ of only 1.57 V, which is comparable with that of RuO₂ (1.59 V), showing a superior catalytic ability to those of other tested electrodes (Table S6) and reported catalysts (Fig. 7b). CoNi-ZIF and MoS₂ nanoparticles have the η₁₀ of 1.63 and 1.73 V, respectively, giving an inferior catalytic ability.

The Tafel plots derived from the polarization curves of all materials reveal the smallest Tafel slope (61 mV dec^{-1}) of MoS$_2$@CoNi-ZIF(3-1) (Fig. 7c and Table S6). Interestingly, although η_{10} of MoS$_2$ NSs is large (1.73 V), a low Tafel slope is obtained (64 mV dec^{-1}), showing that the OER catalytic kinetics of MoS$_2$ is faster than that of CoNi-ZIF, which could further improve the OER performance of MoS$_2$@CoNi-ZIF. In addition, these results reveal that the intrinsic OER catalytic activity of MoS$_2$@CoNi-ZIF(3-1) is superior to that of CoNi-ZIF and MoS$_2$. Also, the OER performance of MoS$_2$@CoNi-ZIF(3-1) outperforms the Co/Ni-based and MOF-derived catalysts (Table S7). The chronopotentiometry curve at a current density of 10 mA cm^{-2} for 48 h is obtained to evaluate the durability of MoS$_2$@CoNi-ZIF(3-1). In Fig. 7d, no significant increase in the overpotential is found during continuous electrolysis for 48 h, showing good stability of MoS$_2$@CoNi-ZIF(3-1). The overpotential is only 77.2% of the initial value at the same conditions for RuO$_2$. The stability of MoS$_2$@CoNi-ZIF(3-1) was also evaluated by continuous sweeps of LSV (scan rate 10 mV s^{-1}, 1.0 M KOH solution) (Fig. 7d inset), and the polarization curve shows a limited decay after 5000 cycles. The outstanding OER activity and good stability of MoS$_2$@CoNi-ZIF(3-1) reveal its potential applications.

3.6. Water splitting performances of MoS$_2$@CoNi-ZIF(3-1)

A two-electrode electrolyzer was assembled and tested for the overall water splitting, in terms of its good bifunctional characteristics of MoS$_2$@CoNi-ZIF(3-1) in both HER and OER (Tables S5 and S7). As shown in Fig. 7e, it shows that only 1.55 V cell potential is required to attain a current density of 10 mA cm^{-2} for MoS$_2$@CoNi-ZIF(3-1), which is comparable to that of commercial Pt/C//RuO$_2$ couple (1.57 V). Also, the catalytic ability of MoS$_2$@CoNi-ZIF(3-1) for the overall water splitting is superior to those of MoS$_2$@CoNi-ZIF(1-1) (1.58 V) and MoS$_2$@CoNi-ZIF(5-1) (1.57 V). These results show that MoS$_2$@CoNi-ZIF (3-1) is one of leading electrocatalysts compared with the known noble metal free bifunctional catalysts such as EG/Co$_{0.85}$Se/NiFe-LDH (1.67 V), Ni-Co-P HNBs (1.62 V), Ni$_{11}$(HPO$_3$)$_8$(OH)$_6$ (1.65 V), (Ni,-Co)$_{0.85}$Se NSAs (1.65 V), and Se-(NiCo)S/OH (1.60 V) (Table S8 and Fig. 7f). The initial activity of MoS$_2$@CoNi-ZIF(3-1) after 40 h is remarkably retained (88.1%) compared with that of the commercial Pt/C//RuO$_2$ couple (73.3% of the initial value). Fig. 7g inset clearly shows gas bubbles produced both on anode and cathode, revealing a great potential of MoS$_2$@CoNi-ZIF(3-1) towards overall water splitting in alkaline solution. The excellent catalytic performances of MoS$_2$@CoNi-ZIF in HER and OER could be attributed to the following reasons: (i) a vertical growth of MoS$_2$ NSs on CoNi-ZIF surface can enhance the HER capacity *via* exposing more active edge sites [55]; (ii) the integration of Co/Ni and MoS$_2$ NSs would change the electronic structure of catalyst, thus improving the intrinsic conductivity [56]; (iii) the presence of metallic states Co and Ni leads to a strong affinity to hydride intermediate during HER for its metallic properties [52] and could serve as the dominating active centers for OER [57]; (iv) the synergistic effect between CoNi-ZIF and MoS$_2$ NSs plays a key role in improving the catalytic performance for HER or OER; (v) the CoNi-ZIF template efficiently prevents MoS$_2$ NSs from assembling, resulting in the unique heterostructure of MoS$_2$@CoNi-ZIF (3-1).

3.7. Post-catalytic structural analyses of MoS$_2$@CoNi-ZIF(3-1)

MoS$_2$@CoNi-ZIF(3-1) used for 48 h of overall water splitting was studied by XPS, XRD, and SEM. The chemical compositions in the XPS survey spectrum do not substantially change after the durability tests were completed (Fig. S12a). The high-resolution XPS spectrum of Co 2p illustrates that the peak intensity of Co^0 species increases (Fig. S12b), suggesting that a part of Co^{2+} in MoS$_2$@CoNi-ZIF(3-1) was reduced to Co^0 species, which is consistent with previous reports [58]. The XPS spectra of Ni, Mo, and S elements do not obviously change compared with the original results (Figs. S12c–e), indicating that Ni, Mo, and S

have the same valence states after the durability tests. These results suggest that MoS$_2$@CoNi-ZIF(3-1) is stable in harsh alkaline environment. The XRD pattern (Fig. S12f) and SEM (Fig. S12g) image of the MoS$_2$@CoNi-ZIF(3-1) after 48 h of durability test reveal that the composition and NS structure remain similar to that of the original material. These results imply the good stability of MoS$_2$@CoNi-ZIF(3-1) during the overall water splitting reaction.

4. Conclusion

In summary, we propose an earth-abundant element electrocatalyst for highly efficient methanol electro-oxidation and overall water splitting, which is achieved by the entrapment of MoS$_2$ layer around a hollow CoNi-ZIF nanostructure. Among the series of MoS$_2$@CoNi-ZIF composites, a considerable enhancement in oxidation peak current density is observed in the electrode based on MoS$_2$@CoNi-ZIF(3-1), thereby exhibiting a superior electrocatalytic activity in MOR. Concurrently, it gives a cell voltage of only 1.55 V at the potential of 10 mV cm^{-2} during the overall water splitting in a two-electrode electrolysis cell in alkaline solution. As compared with other catalysts, the proposed MoS$_2$@CoNi-ZIF(3-1) catalyst has three substantial advantages, (i) multiple catalytic performances for MOR and water splitting in alkaline solution, (ii) feasible synthesis without requiring calcination or other treatments, and (iii) strong synergistic effect among CoNi-ZIF, metal oxide and MoS$_2$, providing MoS$_2$@CoNi-ZIF with both excellent performance and high stability. This work provides a basis for developing new multifunctional catalysts for high-efficiency DMFCs and high-performance clean energy.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcatb.2019.117970.

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